3. WATER QUALITY MONITORING/SAMPLING

This chapter provides information about water quality monitoring and sampling - the first step in the process of generating timely information about water quality and making it available to residents in your area.

The chapter begins with a broad overview of water quality monitoring and then focuses on the monitoring components that were part of the Chesapeake Bay EMPACT Project. The chapter also provides instructions on how to install, operate, and maintain continuous monitoring equipment. Readers primarily interested in an overview of water quality monitoring might want to focus on information presented in this introductory section and the introductory parts of Sections 3.1, 3.2, and 3.3. If you are responsible for the design and implementation of a water quality monitoring project whose goal is to provide timely water quality sample results to the public, you should review Subsections 3.2.1 through 3.2.8. They provide an introduction to the specific steps involved in developing and operating a water quality monitoring project and information on where to find additional guidance. If you are responsible for the design and implementation of a water quality field sampling project, you should review Subsections 3.3.1 through 3.3.2. They provide information on setting up a field sampling program. Subsections 3.3.3 and 3.3.4 provide instructions on how to collect and analyze water samples for various parameters.

3.1 Water Quality Monitoring: An Overview

Water quality monitoring provides information about the condition of streams, lakes, ponds, estuaries, and coastal waters. It can also tell us if these waters are meeting their standards for designed uses, such as for swimming, fishing, or drinking. Water quality monitoring can consist of the following types of measurements:

- *Chemical* measurements of constituents such as nutrients, metals, and oils in water.
- *Physical* measurements of general conditions such as temperature, dissolved oxygen, conductivity/salinity, current speed/direction, water level, water clarity.
- *Biological* measurements of the abundance, variety, and growth rates of aquatic plant and animal life in a water body or the ability of aquatic organisms to survive in a water sample.

You can conduct a variety of water quality monitoring projects, including:

- At fixed locations on a continuous basis.
- At selected locations on an as-needed basis or to answer specific questions.

- On a temporary or seasonal basis (such as during the summer at swimming beaches).
- On an emergency basis (such as after a spill).

Note: As you will read later, the majority of Chesapeake Bay's Water Quality Monitoring Project was conducted on a seasonal basis from April/May through October which corresponds to the times of highest biological activity and it is representative of the SAV growing season in Maryland.

Many agencies and organizations conduct water quality monitoring, including state pollution control agencies, Indian tribes, city and county environmental offices, the EPA and other federal agencies, and private entities, such as universities, watershed organizations, environmental groups, and industries. Volunteer monitors - private citizens who voluntarily collect and analyze water quality samples, conduct visual assessments of physical conditions, and measure the biological health of waters - also provide increasingly important water quality information. The Web site of the EPA Office of Water (http://www.epa.gov/owow/monitoring) is a good source of background information on water quality monitoring. The EPA provides specific information about volunteer monitoring at http://www.epa.gov/owow/monitoring/vol.html.

Water quality monitoring is conducted for many reasons, including:

- Characterizing waters and identifying trends or changes in water quality over time.
- Identifying existing or emerging water quality problems.
- Gathering information for the design of pollution prevention or restoration programs.
- Determining if the goals of specific programs are being met.
- Complying with local, state, and federal regulations.
- Responding to emergencies such as spills or floods.

EPA helps administer grants for water quality monitoring projects and provides technical guidance on how to monitor and report monitoring results. You can find a number of EPA's water quality monitoring technical guidance documents on the Web at: http://www.epa.gov/owow/monitoring/techmon.html. The EPA's Office of Water has developed a Watershed Distance Learning Program called the "Watershed Academy Web." This program, which offers a certificate upon completion, is a series of self-paced training modules that covers topics such as watershed ecology, management practices, analysis and planning. More information about the Watershed Academy Web can be found on the Web at: http://www.epa.gov/watertrain/. The EPA also has a Web site entitled "Surf Your Watershed" which can be used to locate,

use, and share environmental information on watersheds. For more information about the resources available on Surf Your Watershed, please see the following Web site: http://www.epa.gov/surf3. The EPA also has a collection of watershed tools available on the Web at http://www.epa.gov/OWOW/watershed/tools/. The watershed tools deal with topics such as data collection, management and assessment, outreach and education, and modeling.

In addition to the federal EPA resources listed above, you can obtain information about lake and reservoir water quality monitoring from the North American Lake Management Society (NALMS). NALMS has published many technical documents, including a guidance manual entitled *Monitoring Lake and Reservoir Restoration*. For more information, visit the NALMS Web site at http://www.nalms.org. State and local agencies also publish and recommend documents to help organizations and communities conduct and understand water quality monitoring. For example, the State of Maryland maintains a Web site (http://www.dnr.state.md.us/bay/monitoring/) that lists its monitoring strategy for the Chesapeake Bay. State and local organizations in your community might maintain similar listings.

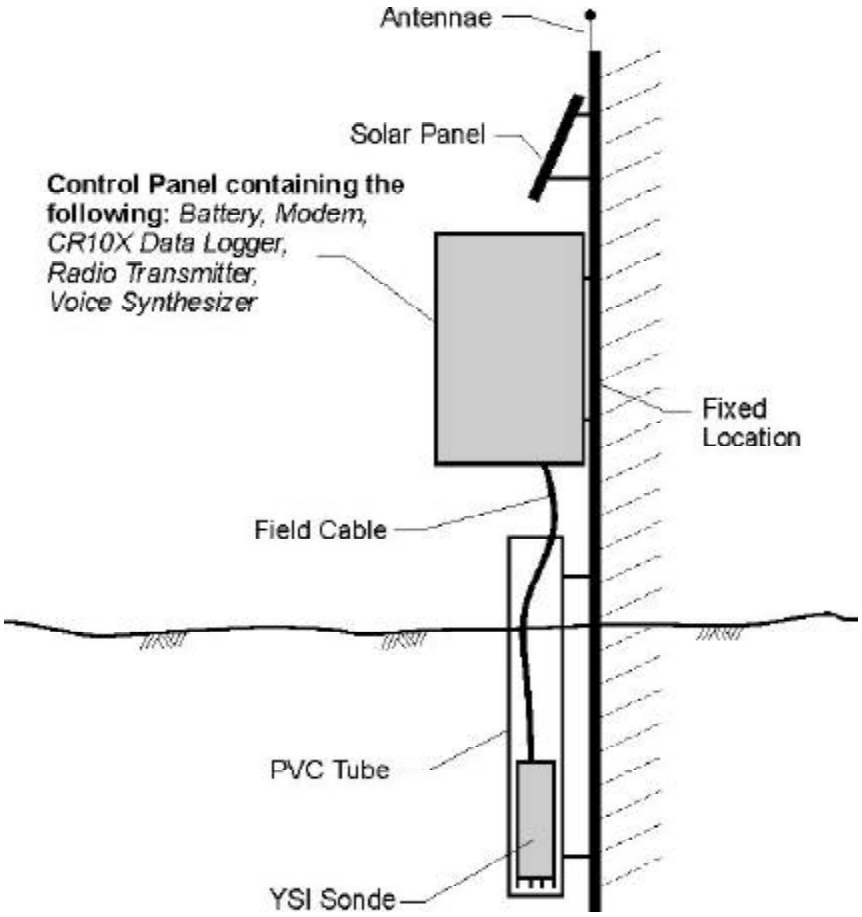
In some cases, special water quality monitoring methods, such as remote monitoring, or special types of water quality data, such as timely data, are needed to meet a water quality monitoring program's objectives. *Timely* environmental data are collected and communicated to the public in a time frame that is useful to their day-to-day decision-making about their health and the environment, and relevant to the temporal variability of the parameter measured. Monitoring is called *remote* when the operator can collect and analyze data from a site other than the monitoring location itself.

3.2 Timely Water Quality Monitoring

The Chesapeake Bay Project monitored a range of water quality parameters including chloropyhll A, dissolved oxygen, nutrients, salinity (conductivity), temperature, and total suspended solids. This information was used to help the State of Maryland, EMPACT project stakeholders and partners, as well as the public, better understand the environmental conditions that can lead to harmful algal blooms, fish kills or the emergence or decline of SAV.

The Chesapeake Bay Project monitored various water quality parameters at eight locations along five rivers feeding into the Chesapeake Bay: Cedar Hall Wharf, Shelltown, Rehobeth (located along the Pocomoke River); Fort McHenry (located along the Baltimore Harbor in the Patapsco River); Cattail Creek and Stonington (located along the Magothy River); Drawbridge (located along the Chicamacomico River); and Decoursey Bridge (located along the Transquaking River). At these locations, the team operated monitoring equipment which monitor water quality using commercially available sondes. A sonde is a group of sensors which transmits timely water quality data to a data acquisition/telemetry system mounted above the water level. Provided below is a schematic showing the general equipment associated with the monitoring station.

Figure 3.1 Monitoring Station



Every 15 minutes, the water quality monitoring station unit equipped with a YSI© 6600 multiprobe water quality sensor measured the following parameters:

- Dissolved oxygen
- DO% Saturation
- Fluorescense/Chlorophyll A
- pH
- Specific conductance/Salinity
- Turbidity
- Water temperature

The remainder of this chapter provides guidelines for designing a water quality monitoring project. It also provides information on the sample collection and analysis procedures used for the field sampling effort.

3.2.1 Designing a Timely Water Quality Monitoring Project

The first step in developing a timely water quality monitoring project is to define your objectives. Keep in mind that timely monitoring might not be the best method for your organization or community. For example, you would not likely need timely monitoring capability to conduct monthly monitoring to comply with a state or federal regulation.

In order to clearly define the objectives of your particular water quality monitoring project, you need to understand the system you are planning to monitor. This means that you need to collect background information about the aquatic system, such as naturally occurring processes, system interactions, system ecology, and human impacts on the system.

Since the Chesapeake Bay monitoring project involves estuarine ecology, the following paragraphs provide some basic background information about this topic.

Estuarine Ecology

Estuaries are bodies of water that are balanced by freshwater and sediment influx from rivers and the tidal actions of the oceans, thus providing transition zones between the freshwater of a river and the saline environment of the sea. The result of this interaction is an ecologically rich environment where estuaries, with large expanses of adjacent marshes and seagrasses, provide a highly productive ecosystem that supports wildlife and fisheries and contributes substantially to the economy of coastal areas. As spawning, nursery, and feeding grounds, estuaries are invaluable to fish and shellfish.

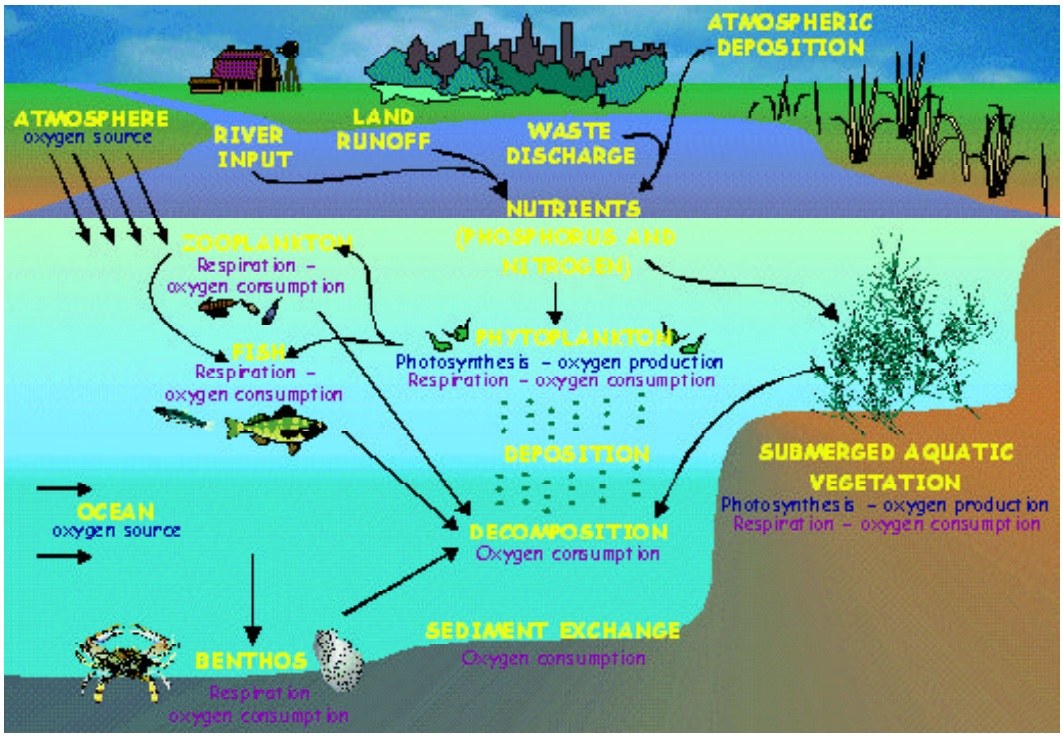
Estuaries and wetland environments are intertwined. Coastal emergent wetlands border estuaries and the coast and include tidal saltwater and freshwater marshes. Coastal wetlands serve as an essential habitat for a diverse range of species. These wetlands are used as a nursery, nesting area, shelter or feeding area by shorebirds, migratory waterfowl, fish, crabs, invertebrates, reptiles, and mammals. Mudflats, salt marshes, mangrove swamps, and barrier island habitats also provide year-round nesting and feeding grounds for abundant populations of gulls, terns, and other shorebirds. Estuaries, marshes and associated watersheds provide habitat for many threatened and endangered species.

Effect of Nutrients on the Chesapeake Bay

Nutrients and organic matter enter the Bay from a variety of sources, including sewage treatment plant effluents, stream inputs, local non-point drainage and direct rainfall on bay waters. A portion of organic matter sinks to the bottom, decomposes and contributes to the development of hypoxic (low oxygen) and anoxic (no oxygen) conditions. Estuarine sediments have the ability to store nutrients that can later allow a "flux" of nutrients from sediments to the water. These fluxes can fuel high rates of

phytoplankton growth and biomass accumulation. Once phytoplankton die, they fall to the bottom where they are decomposed by bacteria. The process of decomposition requires the use of oxygen (see Figure 3.2). Therefore, large amounts of organic matter created by dead phytoplankton blooms can deplete oxygen in bottom sediments which can lead to hypoxia or anoxia. Hypoxia and anoxia are common in eutrophic estuarine systems and threaten our living resources, including SAV, shellfish, fish and other fauna.

Figure 3.2. Components in the Chesapeake Bay That Produce and Consume Oxygen



[Source: http://www.dnr.state.md.us/bay/monitoring/eco/affect.html].

There are usually three overlapping zones in an estuary: an open connection with the sea where marine water dominates, a middle area where salt water and fresh water mix, and a tidal river zone where fresh water dominates. Tidal forces cause the estuarine characteristics to vary. Also variation in the seasonal discharge of rivers causes the limits of the zones to shift, thus increasing the overall ecological complexity of the estuaries.
[Source: http://encarta.msn.com/find/Concise.asp?z=1&pg=2&ti=761570978#s1]

Most of the world's freshwater runoff eventually encounters the oceans in estuaries. Tides or winds help mix the lighter, less dense fresh water from the rivers with the salt water from the ocean to form brackish water. The salinity of brackish water is typically 2 to 10 parts per thousand (ppt), while the salinity of sea water is about 35 ppt. Due mostly to changes in the river flow, the three main estuarine zones - sea water, brackish,

and freshwater - can shift seasonally and vary significantly from one area to another. [Source: http://encarta.msn.com/find/Concise.asp?z=1&pg=2&ti=761570978#s1]

Note: The salinity in the Chesapeake Bay varies from fresh water levels in the upper bay to 20-30 ppt in the low bay.

Harmful Algal Blooms

How An Algal Bloom Can Occur

Ideal conditions for algal growth occurs when you have a combination of algae, high levels of nutrients (e.g., nitrogen and phosphorus), and water temperature and salinity levels conducive to phytoplankton growth in the water body.

In such conditions, the algae consumes the excess nutrient causing a decrease in dissolved nitrogen and phosphorus in the water body.

During the day, overall dissolved oxygen (DO) increases as phytoplankton produces oxygen as photosynthesis occurs.

At night, the DO levels decrease sharply as the algae consumes oxygen.

As the amount of nutrients are depleted, the algae population decreases sharply in what is called a "crash."

As this crash occurs, the dead phytoplankton sinks to the bottom of the water column where they are consumed by decomposers.

Since decomposers require oxygen to break down the algae, DO levels decrease.

Low oxygen levels can be detrimental to fish health. If DO levels drop to below 3 mg/L, fish kills will result!

Microscopic, single-celled plants (phytoplankton) serve as the primary producers of energy at the base of the estuarine food web. Some species of phytoplankton grow very fast, or "bloom," and accumulate into dense, visible patches near the surface of the water. Although the causes of algal blooms are not entirely known, scientists suspect that blooms occur as a result of a combination of high temperatures, a lack of wind, and, frequently, nutrient enrichment. Some algal blooms are called brown tides. While not harmful to humans, they cause serious ecosystem impacts due to decreases in light penetration and dissolved oxygen. Brown tides can cause seagrass die-offs and fish kills. Some algae, such as *Pfiesteria* may produce potent toxins that can cause fish kills and human health problems. Due to the significant health and economic concerns surrounding the outbreaks of toxic *Pfiesteria* that Maryland experienced in 1997, a primary goal of the Chesapeake Bay EMPACT project is to supplement Maryland's larger *Pfiesteria* monitoring efforts.

Pfiesteria

Pfiesteria piscicida is a toxic dinoflagellate that has been associated with fish lesions and fish kills in coastal waters from Delaware to North Carolina. A natural part of the marine environment, dinoflagellates are microscopic, free-swimming, single-celled organisms, usually classified as a type of algae. The vast majority of dinoflagellates are not toxic. Although many dinoflagellates are plant-like and obtain energy by photosynthesis, others, including *Pfiesteria*, are more animal-like and acquire some or all of their energy by eating other organisms.

Pfiesteria normally exists in non-toxic forms, but becomes toxic when it detects an ephemeral substance that live fish excrete or secrete into the water. In its toxic form, *Pfiesteria* secretes toxins into the water which make the fish lethargic. These toxins also injure the fish skin causing bleeding sores and hemorrhaging. North Carolina State University has conducted much research on *Pfiesteria*. For more information, refer to http://www.pfiesteria.org/pfiesteria.

Designing the Chesapeake Bay Project

The Chesapeake Bay Project team's decision to collect timely water quality data was made so that the data would serve as a communications link with the public, providing frequent updates of "real-time" data and emphasizing that the state and EPA are watching 24 hours a day specific areas which could experience harmful algal blooms or other environmental problems. Citizens can access the frequently updated data on the Chesapeake Bay EMPACT Web site (http://mddnr.chesapeakebay.net/newmontech/contmon/index.cfm) which depicts actual conditions being measured in the Pocomoke, Chicamacomico, Transquaking, and Magothy Rivers as well as at Fort McHenry in the Baltimore Harbor.

The project team decided to conduct timely monitoring of water quality to be able to detect algal blooms early and to provide timely environmental information to natural resource and human health protection agencies. Having timely data allows entities to respond quickly to adverse environmental conditions, make appropriate decisions to ensure economic and environmental sustainability of the affected environment, and protect the health of commercial and recreational users.

3.2.2 Selecting Your Monitoring Duration and Frequency

The duration of your monitoring will depend on your project objectives. For example, like the Chesapeake Bay project, if you want to measure the environmental conditions that contribute to *Pfiesteria* outbreaks or other harmful algal blooms, you will want to monitor when those conditions generally occur in your region.

The goal of the Chesapeake Bay EMPACT monitoring program is to have most of the sites collecting data from April through October. These dates correspond to the SAV growing season and are when *Pfiesteria* outbreaks are most likely to occur. However, if your goal is to monitor the effects of freshwater river diversions on a coastal wetland, you may want to monitor water quality year-round.

- If you want to identify existing or emerging water quality problems such as algal blooms, you could tailor your monitoring frequency to collect data often enough to identify problems early in order to take measures to alleviate the problem and warn the public.
- If you want to study seasonal water quality problems, you may want to increase your monitoring frequency during seasons when water quality problems are

more predominant (i.e., low dissolved oxygen levels and associated fish kills during summer months).

It is appropriate to experiment with different monitoring frequencies to optimize your ability to fulfill your project's objectives.

Chesapeake Bay Monitoring Season

- Most of the stations collect data from April through October
- The Fort McHenry station operates year-round and occasionally other sites are maintained year-round to test equipment

The Chesapeake Bay project team programmed its monitoring station to collect water quality data every 15 minutes. This monitoring frequency provides timely environmental data to supplement Maryland's rapid response and comprehensive water and habitat quality assessments of Maryland tributaries that have a potential risk for harmful algal blooms. It also provides the temporal resolution they need to see naturally occurring cyclical changes in various parameters (e.g., Chlorophyll A fluctuations occurring during the daytime and nighttime).

3.2.3 Selecting Water Quality Parameters for Monitoring

The monitoring parameters that you select depend on your project's objectives and the technologies available to you. The Chesapeake Bay/NAIB project teams chose to monitor the following water quality parameters every 15 minutes using the YSI 6600 probe:

- Dissolved oxygen (mg/l)
- DO % saturation (%)
- Fluorescence (%)
- pH
- Salinity (ppt)
- Turbidity (NTU)
- Water temperature (degrees Celsius)

The importance of each parameter is discussed below.

Dissolved Oxygen. Dissolved oxygen (DO) is an indicator of the habitability of estuarine waters for marine life and it is routinely measured by monitoring programs interested in characterizing the eutrophic state of estuaries. DO is recognized as an indicator of the extent of eutrophication because wide fluctuations in DO often result

from increased primary productivity of phytoplankton and may reflect prior nutrient loading. DO concentrations may also vary because of natural processes, such as stratification, depth, wind-induced mixing, and tidal fluxes. DO levels below 5 mg/L can stress organisms while sustained DO levels of less than 3 mg/L can result in fish kills. [Source: http://mddnr.chesapeakebay.net/empact/Current_results_display.cfm.] Sufficient evidence exists that DO < 2 mg/L is extremely stressful to most aquatic organisms. Hypoxia (condition where DO is less than 2 mg/L) increases stress from other factors (e.g., contaminants) on marine organisms, whereas anoxic conditions (DO < 0.1 mg/L) produce toxic hydrogen sulfide which can be lethal to marine biota. Many states require DO concentrations of 4-5 mg/L for estuaries to meet their designated use criteria. Low DO is usually observed from May through September in Chesapeake Bay and is primarily driven by nutrient loading. [Source: http://www.epa.gov/ged/gulf.htm]. Additional information about hypoxia can also be found on the following USGS Web site: http://www.rcolka.cr.usgs.gov/midconherb/hypoxia.html.

DO% Saturation. DO saturation percent shows the level of dissolved oxygen as a percentage of the possible DO the water could contain. Generally, colder water can hold more DO than warmer water. Supersaturation (over 100% DO saturation) can occur when there is a large algal bloom. During the daylight, when the algae are photosynthesizing, they can produce oxygen so rapidly that it is not able to escape into the atmosphere, thus leading to short-term saturation levels of greater than 100%.

Fluorescence. Fluorescence is an indirect measure of the amount of Chlorophyll A in the water column. Since the primary source of the photosynthetic pigment Chlorophyll A is phytoplankton, we can use the fluorescence reading (percent full scale or %FS) as an indicator of phytoplankton populations in the water column. [Source: http://mddnr.chesapeakebay.net/empact/Current_results_display.cfm]

pH. pH is a measure of the hydrogen ion concentration (or acidity) in the water. A pH of 7 is considered neutral. Values lower than 7 are considered acidic and higher than 7 are basic. Many important chemical and biological reactions are strongly affected by pH. In turn, chemical reactions and biological processes (e.g., photosynthesis and respiration) can affect pH. If water becomes either too alkaline or acidic, it can become inhospitable to many species of aquatic life. Lower pH values can also increase the amount of dissolved metals in the water. High pH values can be an indication of an algae bloom.

Salinity. Salinity (or electrical conductivity) is an estimator of the amount of total dissolved salts or total dissolved ions in water. Many factors influence the electrical conductivity/salinity of estuarine water, including the watershed's geology, the watershed's size, wastewater from point sources, runoff from nonpoint sources, atmospheric inputs, evaporation rates, precipitation, fresh water diversion from rivers, tidal surges, and some types of bacterial metabolism. Electrical conductivity/salinity

affects the distribution and health of benthic animals, fish, and vegetation. Both excessively high or low salinities can negatively impact the estuarine ecosystem. Salinity levels are important to aquatic organisms, as some organisms are adapted to live only in brackish or saltwater, while others require fresh water. If the salinity levels get too high, the health of freshwater fish and grasses in the system can be affected.

Turbidity. Turbidity (or backscatter) describes the clarity of the water. Turbidity is a measurement of the amounts of total suspended solids in the water. The particles that make up the turbidity can range from sediment to phytoplankton. In combination with the Chlorophyll A measurements, it can be determined if mineral matter or organics dominate. Predominant organics can be an indication of an algal bloom, which could mean that algae below the zone of light penetration are decaying and consuming oxygen, which in turn, can result in hypoxia that affects bottom dwelling organisms. Measurements of turbidity and backscatter are interrelated in that water with high turbidity measurements also yields high reflectance measurements. Simply put, the more particles that are present in the water, the more light can be scattered back to the sensor. Increased turbidity has several adverse effects on water quality, including the following:

- Turbidity reduces light penetration, which deceases the growth of aquatic plants and organisms. The reduced plant growth reduces photosynthesis, which results in decreased daytime releases of oxygen in the water.
- Suspended particles eventually settle to the bottom, suffocating eggs and/or newly hatched larva, and occupy potential areas of habitat for aquatic organisms.
- Turbidity can also negatively impact fish populations by reducing the ability of predators to locate prey, shifting fish populations to species that feed at the estuary bottom.
- Fine particulate material can affect aquatic organisms by clogging or damaging their sensitive gill structures, decreasing their resistance to disease, preventing proper egg and larval development, and potentially interfering with particle feeding activities.
- Increased inputs of organic particles deplete oxygen as the organic particles decompose.
- Increased turbidity raises the cost of treating surface water for the drinking water supply.

Water Temperature. Water temperature is a product of warming from the sun and air and is another variable affecting suitability of the waterway for aquatic organisms. Water temperature affects metabolic rates and thus has a direct effect on biological activity and the growth of aquatic animal life and aquatic vegetation. Generally, high temperatures (up to a certain limit) increase biological activity and growth, while low temperatures decrease biological activity and growth. For example, high temperatures

in nutrient rich environments promote algal growth and may lead to algal blooms. If water temperatures are consistently higher or lower than average, organisms can be stressed and may have to relocate to areas with a more suitable water temperature. Temperature also affects biological activity by influencing lake water chemistry, such as the oxygen content of the water. Warm water contains less dissolved oxygen than cold water. Low dissolved oxygen levels in the water might not be sufficient to support some types of aquatic life.

3.2.4 Selecting Monitoring Equipment

The type of monitoring method selected depends on your data quality objectives and the purpose of the monitoring. A group of sensors configured together to measure specific physical properties are available as single instruments and are commonly referred to as a sonde, which typically has a single recording unit or electronic datalogger to record the output from the group of sensors. When you select your monitoring equipment, you should carefully consider ease of use, equipment lifetime, reliability, and maintenance requirements. You also might consider using equipment that has been used successfully for similar types of projects.

Note: For descriptions of other EPA EMPACT projects see http://www.epa.gov/ttbnrmrl/Handbks.htm.

The Chesapeake Bay Project team selected the YSI 6600 sensor package to collect timely water quality data. This capability provides opportunities for multi parameter data collection and helped the project team to meet its objectives as described below:

- Archive and display timely water and habitat quality parameters on the Internet for presentation of the data to the general public.
- Provide timely interpretation, as appropriate, relevant to water and habitat quality monitoring data.
- Provide timely environmental data to supplement Maryland's rapid response and comprehensive water and habitat quality assessments of Maryland tributaries that have a potential risk for harmful algal blooms.
- Demonstrate the local government's response to emerging water and habitat quality issues of concern to the public.

Even though the teams use YSI equipment, other manufactures provide similar or alternative equipment. For example, Hydrolab (http://www.hydrolab.com) is another multi-parameter sensor manufacturer. The Maryland DNR uses Hydrolab sensors for some of its other monitoring projects. However, the Chesapeake Bay project team chose the YSI sensor because of its patented Rapid Pulse Dissolved Oxygen Sensor, which provides accurate results without the need for a mechanical stirrer.

Description of a Typical Monitoring Station

The typical monitoring site utilized for the Chesapeake Bay project consists of two types of equipment: monitoring equipment and telemetry equipment. The monitoring equipment consists of a sensor package and a field cable. The telemetry equipment, which is necessary for providing near real-time data to an end user, consists of a datalogger, a battery, a solar panel, modem, and voice synthesizer. The telemetry equipment is discussed in Chapter 4. Information about the monitoring equipment utilized by the Chesapeake Bay team was obtained from the Yellow Springs Instruments, Inc. (YSI) Web site (http://www.ysi.com) and is discussed below.

Sensor Package. The Chesapeake Bay team selected the YSI 6600 sensor package which has a multi-sensor probe, called a sonde, to measure the various water quality parameters. A picture of the YSI 6600 sensor package is shown in Figure 3.3.

The 6600 sonde is YSI's premier unit and can be deployed to measure water quality in fresh, sea, or polluted water at depths up to 200 meters. It is 3.5" in diameter, 20.4" long, and weighs approximately 6 pounds. It has an internal power supply consisting of 8 C-size alkaline batteries. The battery life is approximately 75 days assuming that you buy quality batteries and sample at 15-minute intervals at 25°C. A fully loaded YSI 6600 sonde can measure 11 different parameters and calculate up to 7 additional parameters. The YSI 6600 has 384 kilobytes of logging memory and can store up to 150,000 readings.

Figure 3.3 YSI 6600 Multi-probe sensor

[Photo Courtesy of YSI]

The YSI sondes are warranted for two years; all cables are warranted for one year; and dissolved oxygen, temperature/conductivity, pH, turbidity, and Chlorophyll A probes are warranted for one year.

Also when selecting your equipment, you will want to ensure that it meets generally accepted accuracy and sensitivity requirements. The USGS Web site (http://water.usgs.gov/pubs/wri/wri004252/#pdf) is a good source for background information on calibration and data QA/QC of "real-time" water quality monitoring systems. Table 3.1 shows the YSI sensor calibration requirements and how it compares to the USGS sensor calibration/accuracy requirements.

The information in this Section is summarized from the USGS document titled "Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Site Selection, Field Operation, Calibration, Record Computation, and Reporting" available from the USGS Web site listed above. The USGS guidelines referred to in this document have evolved based on decades of experience with water-quality monitoring. For more information on the YSI 6600's performance specifications, see http://www.ysi.com.

Initially, the Chesapeake Bay team deployed YSI 6920 sondes. The 6920 sonde lacked the capability to measure both turbidity and fluorescence simultaneously because it had only one optical port. As a result, the team could only monitor turbidity. The YSI 6600 is equipped with two optical ports, so when it became available, the team replaced its 6920 sondes with the 6600 so they could also monitor Chlorophyll A which required the additional optical port.

Field Cable. The field cable is a communication link between the YSI 6600 and either a computer or data collection device. The field cable attaches directly to a connector built into the sonde. The other end of the field cable is a military-style 8 pin connector (MS-8). The MS-8 connector plugs directly into YSI 610-D or 610DM display/loggers. Using a YSI 6095B MS-8 to DB-9 adapter, the sonde can be connected directly to a computer for setup, calibration, and uploading files.

PVC Tube. Although not part of the standard YSI-issued sonde equipment, the Chesapeake Bay Team mounts the YSI sonde inside a specially prepared PVC tube. The tube adds further protection for the sonde against the local wildlife, debris, and human tampering. When deploying the sonde inside a PVC tube, the tube should be painted with an anti-fouling coating to prevent algae and barnacles from attaching to the pipe and fouling the DO and fluorescence sensors.

Care should be taken when choosing an antifouling coating, because some will not work in certain conditions. Because Chesapeake Bay's sondes are located in tidal waters, they use an ablative antifouling paint which will remain active as the sonde is continuously re-exposed to water due to tidal forces. If you want to monitor water quality in a fresh water lake where the salinity levels are lower and there are no tidal influences, you should choose a different type of antifouling paint. Antifouling paints can be purchased from boat and marine suppliers.

Other Peripheral Equipment and Software. For the initial setup of the sonde, you will also need a computer with a communications port (DB-9). YSI recommends that the initial setup procedure take place in a laboratory environment rather than in the field. YSI provides a copy of its EcoWatch® for Windows™ (EcoWatch®) which is necessary for programming the sonde. The software is a Windows 3.1 program that works well with Windows 95, 98 and Windows NT. EcoWatch® must be used with an IBM-compatible PC equipped with at least a 386 processor and a 3.5" floppy disk drive. EcoWatch® is discussed further in Chapter 4.

Table 3.1 Performance Specifications for the YSI 6600.

Parameter		YSI Performance Specification	Recommended USGS Performance Specification*
Dissolved Oxygen	Range Resolution Accuracy	0 to 50 mg/l 0.01 mg/l 0 to 20 mg/l: ±2% of reading or 0.2mg/l, whichever is greater; 20 to 50 mg/l:±6% of reading	±0.3 mg/l
% Dissolved Oxygen Saturation	Range Resolution Accuracy	0 to 500% 0.1% 0 to 200%: ± 2% of reading or 2% air saturation, whichever is greater; 200 to 500%: ±6% of reading	Not Addressed
Fluorescence/ Chlorophyll A	Range Resolution	0 to 100% FS 0.1% FS	Not Addressed
pH	Range Resolution Accuracy	0 to 14 units 0.01 unit ±0.2 unit	±0.2 pH units
Conductivity/Salinity	Range Resolution Accuracy	0 to 70 ppt 0.01 ppt ± 1% of reading or 0.1 ppt, whichever is greater	±3%
Turbidity	Range Resolution Accuracy	0 to 1000 NTU 0.1 NTU ±5% of reading or 2 NTU, whichever is greater	±5%
Water Temperature	Range Resolution Accuracy	-5 to 45 °C 0.01 °C ±0.15 °C	±0.2 °C

* See http://water.usgs.gov/pubs/wri/wri004252/#pdf, Table 9.

3.2.5 Siting Monitors

The water quality monitoring location(s) that you select depends on your project's objectives. When you select your monitoring location(s), you should carefully consider the following factors:

- Will the data collected at this ocation(s) fulfill your project's objectives? For example, if you would like a means for early detection of harmful algal blooms,

you need to make sure that you are monitoring parameters that will indicate such.

- Is your community supportive of equipment installation for monitoring in the location(s) you selected?
- Does the monitoring equipment at the selected location(s) present a danger to your community? For example, is the location(s) in an area with heavy boating, swimming, or personal water craft traffic?
- Is your monitoring equipment safe at the selected location(s)? For example, is the equipment protected from vandalism, tampering, or weather-related damage?
- Are there any local, state, or federal regulations that you need to consider in siting the monitor(s)?
- Is access to the monitoring location(s) adequate?

Siting the Chesapeake Bay Locations

You should attempt to place the sonde in an inconspicuous location in a remote area. Human tampering is a risk associated with unattended stations. The Chesapeake Bay team had two options when deciding how to prevent human tampering. One option was to make the station as visible as possible (e.g., place signs stating that monitoring is being conducted, who to report incidents of vandalism to, and visibly securing the sonde). The other option was to hide the station as much as possible. The Chesapeake Bay team chose to hide their monitors or put them in areas where known individuals could easily check the station. To date, the team has not had any problems with human tampering.

The Chesapeake Bay team decided to locate the monitoring system at eight locations (see Table 3.2). Locations were selected because of past fish kills or fish health problems attributable to low DO, or they were adjacent to SAV beds.

Baltimore Harbor - The Maryland Department of Natural Resources is working with the NAIB and Morgan State University to operate a continuous monitoring station in Baltimore Harbor. This station yields water quality and habitat information from a very urban setting adjacent to the Fort McHenry wetland restoration site. The sonde is located inside a PVC pipe attached to a corrugated bulkhead adjacent to the Ft. McHenry wetland restoration site (see Chapter 7).

Pocomoke River - Cedar Hall Wharf - In 1998, the YSI 6600 monitor was anchored to a dock at the Beverly Farm in Cedar Hall Wharf. One surface meter was used at this location. The shallow water location of this meter contrasts with the mid-channel meter placement at Shelltown. The location of this site is such that water quality is still somewhat affected by bay conditions, but not as strongly

as the Shelltown site. Due to the upstream, near-shore placement, water conditions are generally smoother at this site as well.

Table 3.2 Location and Placement of the Chesapeake Bay Monitoring Stations.

Location - Station	Placement	Meter Depth
Baltimore Harbor- Fort McHenry Field Station	Near Shore	One monitor suspended 1 meter below surface
Pocomoke-Cedar Hall Wharf	Near Shore	One monitor suspended 1 meter below surface; Second monitor anchored 1 meter above river bed
Pocomoke-Shelltown	Center Channel	Suspended 1 meter below surface
Pocomoke-Rehobeth	Near Shore	Suspended 1 meter below surface
Magothy-Cattail Creek	Near Shore	Suspended 1 meter below surface
Magothy-Stonington	At the End of a Long Pier	Suspended 1 meter below surface
Chicamacomico-Drawbridge	Center Channel (narrow channel area)	Suspended 1 meter below surface
Transquaking-Decoursey Bridge	Center Channel	Suspended 1 meter below surface

Pocomoke-Shelltown - The original location (1998) of the Shelltown station was in the Pocomoke River on a dock near Shelltown. In 1999, the station was moved to a piling driven into the sediment slightly downstream at Williams Point (near the Pocomoke Sound). Williams Point is one of the Pocomoke River sites of the 1997 *Pfiesteria* outbreaks resulting in fish kill estimated at 10,000 to 15,000 fish. This station is more affected by bay conditions than further upstream conditions. Due to its proximity to the bay, salinity levels at this station are generally higher than at other stations.

Pocomoke-Rehobeth -The site was installed in 1999. The YSI 6600 monitor is anchored to a piling near a retaining wall at Rehobeth. This area is close to shore and somewhat protected from wave action and high rates of water flow. Being the furthest away from the bay, this site is the least affected by bay water quality fluctuations. Due to its distance from the Bay, this site experiences lower salinity levels than the other continuous monitoring sites.

Magothy-Stonington - This site was installed in 2000. The YSI 6600 monitor is anchored at the end of a long pier located in a residential area. The pier is maintained by a home owners association so MD DNR had to obtain permission to place the station there.

Magothy-Cattail - This site was installed in 2000. The YSI 6600 monitor is anchored on the side of a residential pier. MD DNR obtained permission from the home owner to place the station at this site. This station is located in an inlet area where the water does not circulate well and typically shows very low DO levels. A non-toxic *Pfiesteria* piscicida outbreak was confirmed in 1999 near this site. Once the EMPACT project ended, this monitor was moved to the Whitehurst location on the Magothy River.

Chicamacomico-Drawbridge - This site was installed in 2000. The YSI 6600 monitor is located on the side of a small fishing pier. The location is fairly remote but there is a small boat manufacturing company located next to the pier. In 1997, a portion of the Chicamacomico River near Drawbridge Road in Dorchester County was closed after a significant number of menhaden were found in distress and dying with *Pfiesteria*-like lesions. Results of water samples from the Chicamacomico indicated the presence of toxic levels of *Pfiesteria piscicida.*

Transquaking–Decoursey Bridge - The YSI 6600 monitor is anchored on the side of a small bridge in a remote area. To prevent tampering, the team made an effort to position the station so that it could not easily be seen from the road or bridge. This station was located near the site of a non-toxic *Pfiesteria* outbreak in 1999. Once the EMPACT project ended, this monitor was moved to the Severn river to collect similar data.

3.2.6 Installing the Monitoring System

This section discusses some of the basic preparation and installation procedures for the monitoring system. Detailed step-by-step installation procedures for the monitoring equipment are available from the YSI's Environmental Monitoring Systems Operations Manual for 6-Series sondes. The user's manual for the YSI 6-Series sondes can be downloaded from the Yellow Springs Instruments, Inc. Web site at http://www.ysi.com. If you purchase a YSI sonde, you will receive a manual.

Unpack and Inspect the Monitoring Equipment

The first step to installing the monitoring system is to unpack and inspect the equipment. As soon as you receive the equipment, you should do the following:

- Remove the equipment from the shipping boxes or containers.
- Using the enclosed packing slip, perform an inventory of all items. If you are missing any items, contact the manufacturer immediately.
- Conduct a thorough visual inspection of all items. If you observe any damage, contact the manufacturer and the carrier.

Prepare the Sonde for Use

The second step to installing the monitoring system is to prepare the sonde for calibration and operation. You should perform the following basic procedures:

- Install the DO membrane on the DO probe.
- Install the other probes (e.g., turbidity, conductivity, temperature, pH etc.).
- Provide power for the sonde (e.g., install batteries or external power supply).
- Connect the field cable to the sonde.

Install Software

The third step to installing the monitoring system is to install the necessary computer software. As stated earlier, YSI recommends that the software be installed on a computer in a laboratory setting for the initial setup of the sondes.

Two different types of computer software can be used with YSI's environmental monitoring systems. EcoWatch® for Windows™ or PC6000, which is a DOS-based software. The Chesapeake Bay team uses EcoWatch® for Windows™.

To get started with EcoWatch® for Windows™, perform the following steps:

- Install EcoWatch® for Windows™ on your computer. Place Disk 1 of EcoWatch® in your 3.5" drive, select "Run" and type "a:\setup.exe" at the prompt. Click on "OK" and the display will indicate that EcoWatch® is being installed. Follow the instructions on the screen after the installation is complete.
- Connect your field cable (and sonde) to a communication port on the computer where EcoWatch® is installed.
- Click on the EcoWatch® icon on your computer to begin running the software.
- Select the **Sonde** icon on the Ecowatch tool bar and then select the proper communication port to which your sonde is connected (e.g., 1 or 2).
- Ensure that the baud rate is 9600 on the **Comm** menu.
- Specify a parallel port to select a printer.
- Select **Sonde** from the EcoWatch® menu to communicate between your computer and the sonde. Once the proper communication port is selected, a window showing a # sign will appear. Type "menu" after the # sign and press **Enter** to get the Sonde **Main Menu**. From the Sonde **Main Menu**, you can set up the date and time, choose communication baud rates, select page lengths, identify your instruments (sondes), enable the sondes' sensors, and develop a report to show the parameters you want to see when you collect your

data. For detailed instructions on these procedures refer to the YSI Environmental Monitoring Systems Operations Manual for 6-Series sondes.

You may encounter some problems with the communication between the sonde and the computer. Possible causes and recommended actions to correct the problem are provided in the Table 3.3.

Table 3.3 Troubleshooting Communication Problems Between the Sonde and Computer.

Possible Cause	Recommended Actions
Sonde has no power	Check the batteries or the power source
Field Cable connection is loose	Check both ends of the field cable
Damaged Connectors	Check the pins at both ends; they should be straight, dry and clean
Com port not selected	Change to other port or try another computer or display/logger

Calibrate the Probes on the Sonde

The next step to installing the monitoring system is to calibrate and check the sonde according to the manufacturer's instructions. Various reagents and calibration standard solutions are required to calibrate the various probes. YSI makes a calibration cup for their sondes which serves as a chamber for all calibrations and minimizes the amount of reagents required to calibrate the sonde. You may use laboratory glassware instead to perform the calibrations; however, you should take special precautions to avoid damaging the probes.

Program the Sonde for Monitoring

After the sensors have been enabled and calibrated and a report is developed to display your monitoring results, you are ready to program the sonde for your unique monitoring conditions. Selecting **1-Run** from the main menu will allow you to set up your parameters for your study. You have two monitoring options: "discrete sample" and "unattended sample." The monitoring frequency for discrete sampling is likely to be for only seconds in order to obtain short term or "snapshot" results as you move from site to site during the day. The monitoring frequency for unattended sampling is usually longer (e.g., minutes) because the sonde will be deployed for days or weeks at a time. This is where you specify your sampling interval (e.g., seconds or minutes), the sampling start date, the sampling start time, the duration for sampling, and which parameters to log.

Once you program your monitoring parameters, the internal software of the sonde will automatically calculate the expected battery life and the amount of time to fill the internal memory of the sonde. You can use this information to determine if your monitoring program should be adjusted or if you need new batteries, etc.

Once you finish programming the sonde you can begin collecting monitoring data. The data collected by the sonde is saved in a .dat file in the sonde's memory (386 kilobytes max.).

Note: The Chesapeake Bay project programs their sondes for unattended sampling.

3.2.7 Using EcoWatch® to Capture, Upload and Analyze Data

This section discusses the basic steps for using EcoWatch® to capture, upload, and analyze data collected by the sonde. The procedures listed below were summarized from the YSI's Environmental Monitoring Systems Operations Manual for 6-Series sondes. You will need to refer to this manual for detailed step-by-step operation guidance.

Capturing Data

EcoWatch® can be used to capture real-time data to your computer's hard drive or to a disk. To use this function, you will need to do the following:

- Connect the sonde's field cable to your computer's communications port.
- Run the EcoWatch® software.
- Click on the **Sonde** icon and choose the correct communications port.
- From the sonde's **Main** menu, press **1-Run** and then **1-Discrete Sample**.
- Verify that the sample interval is set to the correct value.
- Open the **Real-Time** menu, click on **New** and select the directory where you want the data transferred. Name the file giving it the extension **.RT**.
- Click **OK** and wait for data transfer to begin. EcoWatch® will automatically save the data as a .DAT file in your designated directory.
- When finished, open the **Real-Time** menu, choose **Close**, and click on **OK**.

Uploading Data

EcoWatch® can also be used to retrieve data already stored in the sonde's memory (i.e., sondes which have been running unattended). To use this function, you will need to perform the following procedures:

- Connect the sonde's field cable to your computer's communications port.
- Run the EcoWatch® software.
- Click on the **Sonde** icon and choose the correct communications port.
- Enter the **File** menu, and select **1-Directory** to view the files currently stored in the sonde's memory.
- Select **2-Upload** to upload the data to your computer.
- Select **1-Proceed** and choose a file transfer protocol (PC6000 is recommended because it is faster). A status box will appear on the screen indicating the status of the file transfer.
- Select **4-View File** to see the data in any file currently stored in the sonde's memory.
- If you want to *permanently* delete the data from the sonde's memory select **6-Delete**.

Analyzing Data

Once you have uploaded the sonde's data to your computer, you can use EcoWatch® to view, plot, manipulate and report the data. For example, when you select **File** and **Open** to open a data file, you can see a one-page plot showing line graphs of all the data logged on your sonde. Based on your selection, you can view as many (or as few) graphs as you prefer. You can also set time limits to view data within a specified time frame (e.g., a day as opposed to a week). Viewing data using EcoWatch® is useful because you can see daily variations in parameters such as temperature and dissolved oxygen. You may see obvious erroneous data such as flat-line data where the sonde was out of the water just prior to deployment. While in the graph mode, you can put your cursor on the graph and hold down the right mouse button causing a vertical dotted line to appear. The instantaneous value will appear where the vertical line crosses the graph. You can move the mouse to scan the graph and read the corresponding instantaneous values. EcoWatch® allows you to view data in a tabular mode as well. The software also has a **Statistics** function which will calculate minimum, maximum, mean, and standard deviation information for each activated parameter.

Saving, Importing, Exporting, and Printing Data

EcoWatch® has various options under its **File** menu to save, import, export, and print data. You can modify and save or rename a file. Once saved, you can export a file in a Comma & ' ' Delimited format (.CSV) or print it to a compatible printer. EcoWatch® has a **Help** function which will explain these features.

3.2.8 Maintaining the Monitoring System

The scheduled maintenance activities for your monitoring system will likely involve cleaning and calibration of your water quality monitoring sensors and replacement of desiccant for the water level sensor. Maintenance frequency is generally governed by the fouling rate of the sensors and this rate varies by sensor type, hydrologic environment, and season. The performance of temperature and specific conductance sensors tends to be less affected by fouling, whereas the dissolved oxygen, pH, and turbidity sensors are more prone to fouling. The use of wiper or shutter mechanisms on modern turbidity instruments has decreased the fouling problem significantly. For stations with critical data quality objectives, service intervals may be weekly or more often. Monitoring sites with nutrient-enriched waters and moderate to high temperatures may require service intervals as frequently as every third day. In cases of severe environmental fouling, the use of an observer for servicing the water quality monitor should be considered. In addition to fouling problems, physical disruptions (such as recording equipment malfunction, sedimentation, electrical disruption, debris, or vandalism) also may require additional site visits. The service needs of water quality monitoring stations equipped with telemetry can be recognized quickly, and the use of satellite telemetry to verify proper equipment operation is recommended. The USGS Web site (http://water.usgs.gov/pubs/wri/wri004252/#pdf) is a good source for background information on operation and maintenance of near-real time water quality monitoring systems. The information in this Section is summarized from the USGS document titled "Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Site Selection, Field Operation, Calibration, Record Computation, and Reporting." This document is available from the USGS Web site listed above.

Chesapeake Bay Project Maintenance Activities

Because of the potential fouling of the dissolved oxygen sensor, the Chesapeake Bay team decided that all stations should be maintained weekly May through October. Personnel from the Chesapeake Biological Laboratory (CBL) maintained the three stations located on the Pocomoke River once each week. MD DNR personnel maintained the four stations located on the Magothy, Chicamacomico, and Transquaking Rivers each week, and similarly the Baltimore Aquarium personnel maintained the station located at Fort McHenry once each week. In the event of physical disruptions (such as recording equipment malfunction, sedimentation, electrical disruption, debris, or vandalism), the Chesapeake Bay/NAIB teams would conduct additional site visits. Also during weekly visits (May through October), the teams collect water samples to be analyzed later for nutrient analysis (see Section 3.3). Although some of the stations are not close to each other, the teams can typically service up to four monitoring stations in a single day.

Each team had two YSI 6600 sondes for each monitoring station. During the weekly field visit, the team removed the deployed sonde from the station and replaced it with

a freshly calibrated sonde. Both the field monitor being retrieved and the replacement field monitor were recording simultaneous data for beginning and endpoint comparison. Prior to deploying the fresh sonde, the team used a long brush to scrub the inside of the PVC tube where the sonde is placed. The team was careful to switch the sondes prior to a monitoring event that occurs in 15 minute intervals to avoid interruptions in the data collection.

The sondes were retrieved from each monitoring station and wrapped in wet towels to keep the DO membrane in a 100% saturated-air environment. The sondes continued to log data while out of the water so they could achieve equilibrium for the post calibration test. The sondes were taken back to the laboratory where they continued to log data overnight in order to equilibrate. Usually the next day, the team performed post calibration tests for each of the sensors to determine if they operated correctly while in the field. The pH, turbidity, conductivity and Chlorophyll A sensors were calibrated against known standard solutions. The calibration of the dissolved oxygen sensor was conducted in the controlled environment of the team's laboratory. Calibration of the temperature sensor was not required.

In addition to the post calibration test, the team used EcoWatch® to upload and visually inspect the data collected by the sonde (see Chapter 4 for further discussions). The team checked the sonde's batteries and inspected and cleaned the various sensors according to the manufacturer's instructions. The sensors were carefully cleaned to remove algae and any other organisms that could foul the sensors. The team typically spent one half to a full day calibrating, inspecting, and cleaning the sonde's sensors.

The detailed maintenance requirements and procedures for the monitoring equipment are available from the user's manuals of the individual pieces of equipment. The user's manual for the YSI 6600 sensor package can be downloaded from the Yellow Springs Instruments, Inc. Web site at http://www.ysi.com.

Table 3.4 Common Troubleshooting Issues and Actions

Symptoms	Possible Cause	Action
Dissolved Oxygen reading unstable or inaccurate	Probe not properly calibrated	Follow DO calibration procedures
	Membrane not properly installed or punctured	Follow setup procedure
	DO probe electrodes require cleaning	Follow DO cleaning procedure
	Water in probe connector	Dry connector; reinstall probe
	Algae or other contaminant clinging to probe	Rinse DO probe with clean water
	Barometric pressure is incorrect	Repeat DO calibration procedure
	Calibrated at extreme temperature	Recalibrate at/near sample temperature
	DO charge too high (>100): (1) Anode polarized (tarnished) (2) Probe left on continuously	Enable DO charge parameter in sonde report menu. Run sonde, if charge is over 100, recondition probe. Follow DO cleaning procedure.
	DO charge too low (<25); insufficient electrolyte.	Replace electrolyte and membrane
	DO probe has been damaged	Replace probe
	Internal failure	Return sonde for service
pH, chloride, ammonium, or nitrate readings are unstable or inaccurate. Error messages appear during calibration	Probe requires cleaning	Follow probe cleaning procedure
	Probe requires calibration	Follow calibration procedures
	pH probe reference junction has dried out from improper storage	Soak probe in tap water or buffer until readings become stable
	Water in probe connector	Dry connector; reinstall probe
	Probe has been damaged	Replace probe
	Calibration solutions out of spec or contaminated	Use new calibration solutions
	Internal failure	Return sonde for service
Level Sensor unstable or inaccurate	Desiccant is spent	Replace desiccant
	Level sensor hole is obstructed	Follow level sensor cleaning procedure
	Level sensor has been damaged	Return sonde for service
	Internal failure	Return sonde for service
Conductivity unstable or inaccurate. Error messages appear during calibration	Conductivity improperly calibrated	Follow recalibration procedure
	Conductivity probe requires cleaning	Follow cleaning procedure
	Conductivity probe damaged	Replace probe
	Calibration solution out of spec or contaminated	Use new calibration solution
	Internal failure	Return sonde for service
	Calibration solution or sample does not cover entire sensor	Immerse sensor fully
Installed probe has no reading	Sensor has been disabled	Enable sensor
	Water in probe connector	Dry connector; reinstall probe
	Probe has been damaged	Replace probe
	Report output improperly set	Set up report output
	Internal failure	Return sonde for service
Temperature unstable or inaccurate	Water in connector	Dry connector; reinstall probe
	Probe has been damaged	Replace probe
Turbidity probe unstable or inaccurate. Error messages appear during calibration	Probe requires cleaning	Follow probe cleaning procedure
	Probe requires calibration	Follow calibration procedure
	Probe has been damaged	Replace probe
	Water in probe connector	Dry connector; reinstall probe
	Calibration solutions out of spec	Use new calibration solutions
	Wiper is not turning or is not synchronized	Activate wiper. Assure rotation. Make sure set screw is tight
	Wiper is fouled or damaged	Clean or replace wiper
	Internal failure	Return probe for service

3.3 Water Quality Field Sampling

3.3.1 Purpose of Field Sampling

The team also collected water samples during their weekly visits. The samples were collected to analyze for chemical properties that cannot be measured by the automated field monitors, to calibrate the field monitors, and to verify the accuracy of transmitted and downloaded data.

3.3.2 Parameters Measured from Field Samples

The following parameters were measured from the samples collected during weekly maintenance visit:

- Chlorophyll A
- Nutrients
  - Particulate carbon
  - Particulate nitrogen
  - Dissolved organic carbon
  - Dissolved organic nitrogen
  - Dissolved organic phosphorus
  - Dissolved inorganic phosphorus
  - Particulate phosphorus
  - Nitrate-Nitrite
  - Nitrite
  - Ammonium
- Total suspended solids

The importance of each of these parameters is discussed below.

Chlorophyll A

Chlorophyll A can be an indicator of the first level response to nutrient enrichment. Measurements of chlorophyll A (via fluorescence) in the water column represent the standing stock or biomass of phytoplankton. Blooms of phytoplankton often indicate that an estuary is undergoing eutrophication. In some estuaries, there is a good correlation between nitrogen loadings from various sources and concentrations of Chlorophyll A. In other estuaries, however, the relationship does not hold and it is possible, in fact, for an estuary to receive heavy loads of nitrogen and yet not exhibit increases in phytoplankton biomass. Other factors such as light limitation, depth of the mixing zone, flushing rates, and contaminants may affect the growth of phytoplankton.

Nutrients

Particulate Carbon and Dissolved Organic Carbon. Organic matter plays a major role in aquatic systems. It affects biogeochemical processes, nutrient recycling, biological availability, chemical transport and interactions. It also has direct implications in the planning of wastewater treatment and drinking water treatment. Organic matter is typically measured as total organic carbon (TOC) and dissolved organic carbon (DOC), which are essential components of the carbon cycle. [Source: BASIN Water Quality Terminology, http://bcn.boulder.co.us/basin/natural/wqterms.html]

Particulate Nitrogen, Dissolved Organic Nitrogen, Nitrate-Nitrite, Nitrite, and Ammonia. Nitrogen is required by all organisms for the basic processes of life to make proteins, to grow, and to reproduce. Nitrogen is very common and found in many forms in the environment. Inorganic forms include nitrate (NO_3) and nitrite (NO_2). Organic nitrogen is found in the cells of all living things and is a component of proteins, peptides, and amino acids. Excessive concentrations of nitrate, nitrite, or ammonia can be harmful to humans and wildlife. Nitrate, nitrite, and ammonia enter waterways from lawn fertilizer run-off, leaking septic tanks, animal wastes, industrial waste waters, sanitary landfills and discharges from car exhausts. [Source: BASIN Water Quality Terms, http://bcn.boulder.co.us/basin/natural/wqterms.html]

Particulate Phosphorus, Dissolved Organic Phosphorus, Dissolved Inorganic Phosphorus. Phosphorus is a nutrient required by all organisms for the basic processes of life. Phosphorus is a natural element found in rocks, soils, and organic material. Its concentration in clean water is generally very low; however, phosphorus is used extensively in fertilizer and other chemicals, so it can be found in higher concentrations in areas of human activity. Phosphorus is generally found as phosphate (PO_4^{-3}). High levels of phosphate, along with nitrate, can overstimulate the growth of aquatic plants and algae, resulting in high dissolved oxygen consumption, causing death of fish and other organisms. The primary sources of phosphates in surface water are detergents, fertilizers, and natural mineral deposits. [Source: BASIN Water Quality Terms, http://bcn.boulder.co.us/basin/natural/wqterms.html]

Total Suspended Solids (TSS). TSS refers to matter (e.g., silt, decaying plant and animal matter, industrial wastes, and sewage) suspended in water, and is related to both specific conductance and turbidity. High levels of TSS in water can have detrimental effects because it reduces sunlight passing through the water, which reduces the rate of photosynthesis, which lowers the amount of dissolved oxygen in the water. [Source: BASIN General Information on Solids, http://bcn.boulder.co.us/basin/data/FECAL/info/TSS.html]

3.3.3 Sample Collection Procedures

The team used an Alpha™ water bottle to collect the field samples. To collect the sample, the 2 liter Alpha™ bottle is opened and horizontally-mounted on a line. The Alpha™ bottle is lowered into the water and positioned at probe depth (i.e., 1 meter below the surface). Once in position, a small stainless steel weight (called a messenger) which is attached to the line), is released and slides down the line to the Alpha™ bottle. The impact of the messenger causes the Alpha™ bottle to close thereby collecting a raw water sample. The Alpha™ bottle is removed from the water. The results from the analysis of the water sample are related to readings from the field monitor that correspond to both the beginning and end-point readings for respective data records.

Note: An additional Hydrolab sonde and data display are also taken to the field to obtain instantaneous temperature, salinity, and DO readings.

Raw sample water is drawn immediately from the Alpha™ bottle to a 500-ml Nalgene bottle for further processing (see Figure 3.4). A standard thermometer is placed in the Nalgene bottle to equilibrate while additional raw sample water is drawn from the Alpha™ bottle for Winkler dissolved oxygen determinations. From the Alpha™ bottle, one clear glass 300-ml BOD bottle is filled and preserved immediately.

Figure 3.4 Water Sampling Alpha™ Bottle

Note: For more information on the use and costs of Alpha™ bottles and other peripheral equipment see http://www.wildco.com/liquid.html.

Next, raw water in the 500 ml Nalgene bottle is shaken gently. Using a vacuum pump, flask and filter apparatus, a measured quantity is filtered through a pre-combusted filter

pad (Whatman 25 mm diameter 0.7 μm particle retention) for particulate carbon and particulate nitrogen analysis (1 pad for each). Pads are folded and placed in aluminum foil pouches on ice.

Figure 3.5 GF/F Filter Being Placed in a Foil Pouch

The filter apparatus is then exchanged to accommodate larger filter pads. Raw water in the 500 ml Nalgene bottle is shaken gently, a measured quantity is filtered through a 47 mm filter pad for Chlorophyll A analyses and the pad is folded and placed in an aluminum foil pouch on ice.

At this point, the resulting filtrate is decanted and a portion used to rinse respective containers for the following samples. A measured quantity of filtrate is retained in a capped test tube for dissolved organic nitrogen and phosphorus analyses. Three auto-analyzer (AA) vials are filled for nitrite-nitrate, nitrite, and ammonium analyses. A capped Teflon® tube is filled for dissolved organic carbon analysis.

The remaining raw water in the 500-ml Nalgene bottle is shaken and a measured quantity is filtered through a pre-weighed filter pad (Whatman 47 mm diameter GF/F filter pad) for particulate phosphorus and total suspended sediment analysis (1 pad for each). Pads are rinsed twice with deionized water, folded and placed in aluminum foil pouches on ice (see Figure 3.5).

Remaining water in the Alpha™ bottle is shaken and a portion is used to fill a 500-ml Nalgene bottle for phytoplankton species composition analysis. The sample is preserved using 5 ml Lugol's solution (a strong iodine solution).

All on-site sample processing is completed within 30 to 45 minutes of water collection. The three aluminum pouches, three AA vials, one Teflon® tube and one test tube from

each site remain on ice during the transport back to the laboratory, where they are frozen until later laboratory analysis. The samples processed by the MD DNR and Baltimore personnel are sent by courier to the CBL for analysis.

3.3.4 Sample Analysis Procedures

When CBL receives the processed samples, they perform a variety of analyses. Winkler titration procedures are performed and water samples for nutrient and Chlorophyll A determination are processed and sent out for laboratory analysis. Beginning and end-point Winkler dissolved oxygen determinations are completed and used for calibration of instrument measurements. Since laboratory analyses results of Chlorophyll A and turbidity measurements require a longer time for completion, calibration of those parameters is completed at a later time. All time-series data are edited to reflect any calibration corrections or deletions as needed and documented.

Standard oceanographic and estuarine methods of chemical analysis are used for all determinations of dissolved and particulate materials. The water quality techniques used by CBL to conduct the water quality analyses are described below. Further discussion on these techniques are discussed in the Nutrient Analytical Services Laboratory's Standard Operating Procedures found at http://www.cbl.cees.edu/nasl/documents/SOP.pdf.

Determination of *ammonia* is by the Berthelot Reaction in which a blue-colored compound similar to indophenol forms when a solution of ammonium salt is added to sodium phenoxide, followed by the addition of sodium hypochlorite. The addition of potassium sodium tartrate and sodium citrate solution prevents precipitation of hydroxides of calcium and magnesium. This is an automated colorimetric technique. The reaction forms a blue color measured at 630 nm using the Technicon TrAAcs-800 Nutrient Analyzer. [Methodology: Technicon Industrial Method No. 804-86T. August 1986. Technicon Industrial Systems. Tarrytown, New York, 10591]

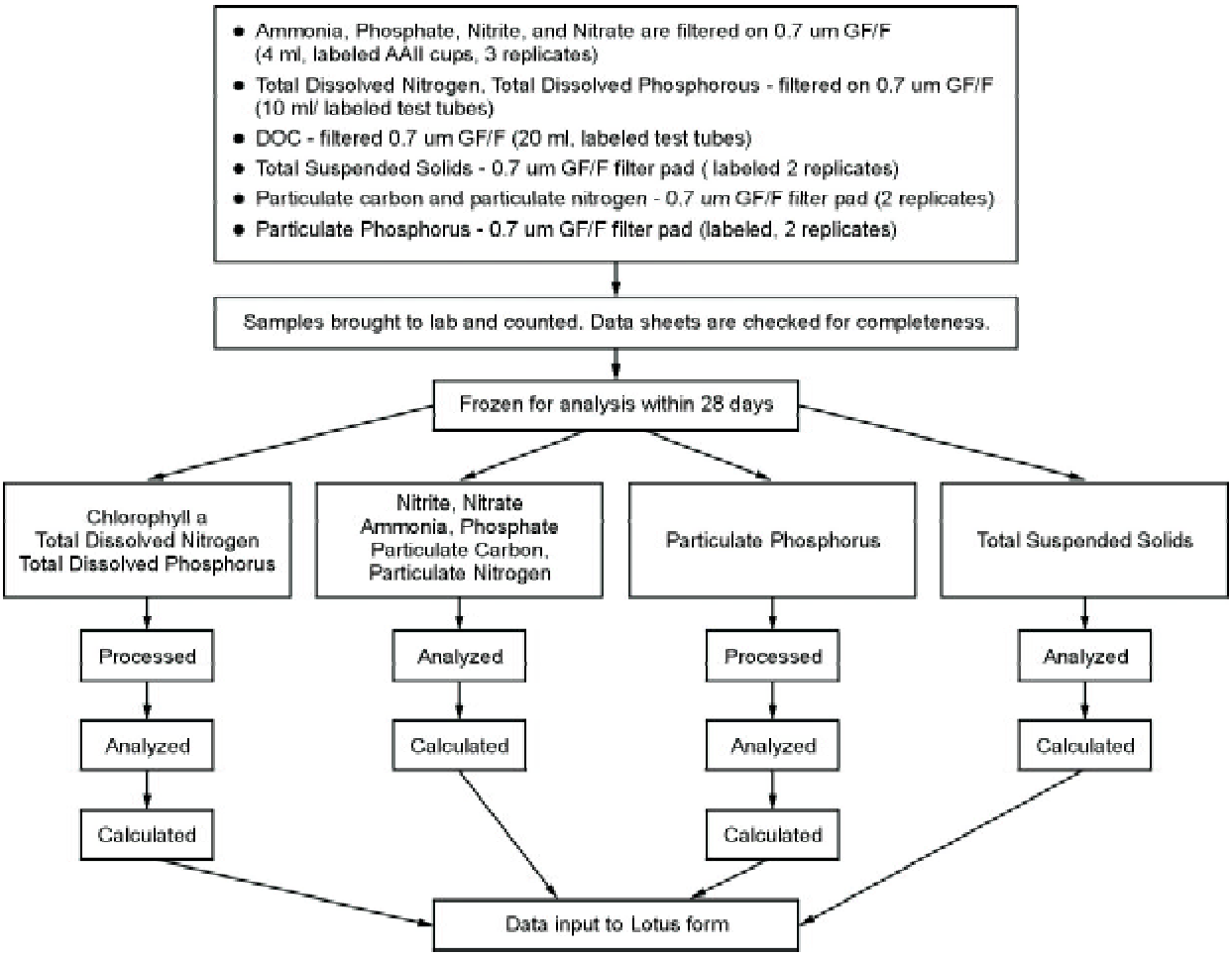
Nitrate reacts under acidic conditions with sulfanilamide to form a diazo compound that couples with N-1-naphthylethylenediamine dihydrochloride to form a reddish-purple azo dye measured at 520 nm using the Technicon TrAAcs-800 Nutrient Analyzer. [Methodology: Technicon Industrial Method No. 818-87T. February 1987. Technicon Industrial Systems. Tarrytown, New York, 10591]

For *Nitrite* + *Nitrate* measurement, filtered samples are passed through a granulated copper-cadmium column to reduce nitrate to nitrite. The nitrite (originally present plus reduced nitrate) then is determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a colored azo dye that is measured at 550 nm using a Technicon AutoAnalyzer II. Nitrate concentration is obtained by subtracting the corresponding nitrite value from the nitrite + nitrate concentration. [Technicon Industrial Method No. 158-71 W/A † Tentative. 1977.

Technicon Industrial Systems. Tarrytown, New York, 10591 and USEPA. 1979. Method No. 353.2 *in* Methods for Chemical Analysis of Water and Wastes. United States Environmental Protection Agency, Office of Research and Development. Cincinnati, Ohio. Report No. EPA-600/4-79-020, March 1979.]

Methods for measuring dissolved organic carbon, nitrogen and phosphorus are described below. All procedures require the addition of potassium persulfate to a sample, which when under heat and pressure, breaks down the organic constituents to inorganic forms. Inorganic fractions then are subtracted from the total dissolved sample to yield the dissolved organic concentration. See Figures 3.6, 3.7 and 3.8.

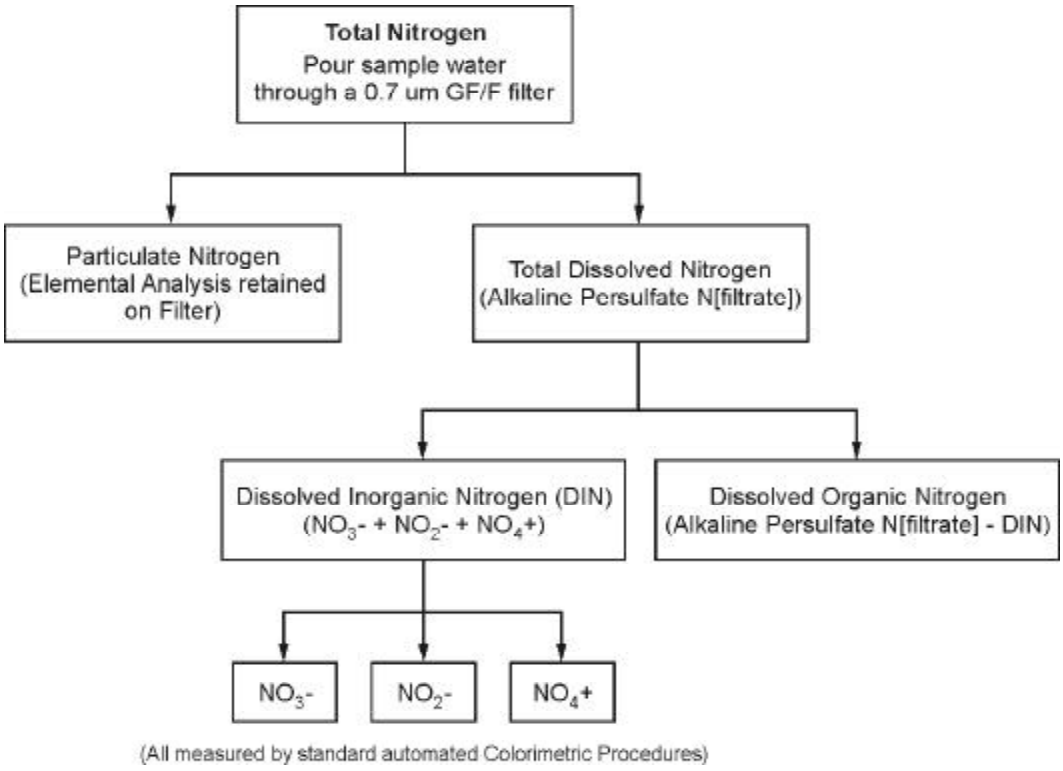
Figure 3.6 General Laboratory Procedures for Nutrient Analyses.



The method for determining *Total Dissolved Nitrogen* and *Phosphorus* is a persulfate oxidation technique for nitrogen and phosphorus where, under alkaline conditions, nitrate is the sole nitrogen product and phosphate is the sole phosphorus product. Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex which is reduced to an intensely blue-colored complex by ascorbic acid. Color is

proportional to phosphorus concentration. Digested samples are passed through a granulated copper-cadmium column to reduce nitrate to nitrite. The nitrite then is determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a colored azo dye. Color is proportional to nitrogen concentration. Color is measured by a Techni-con AutoAnalyzer II. [D'Elia, C.F., P.A. Steudler and N. Corwin. 1977. Determination of Total Nitrogen in Aqueous Samples using Persulfate Digestion. Limnol. Oceanogr. 22:760-764. and Valderrama, J.C. 1981. The Simultaneous Analysis of Total Nitrogen and Total Phosphorus in Natural Waters. Mar. Chem. 10:109-122]

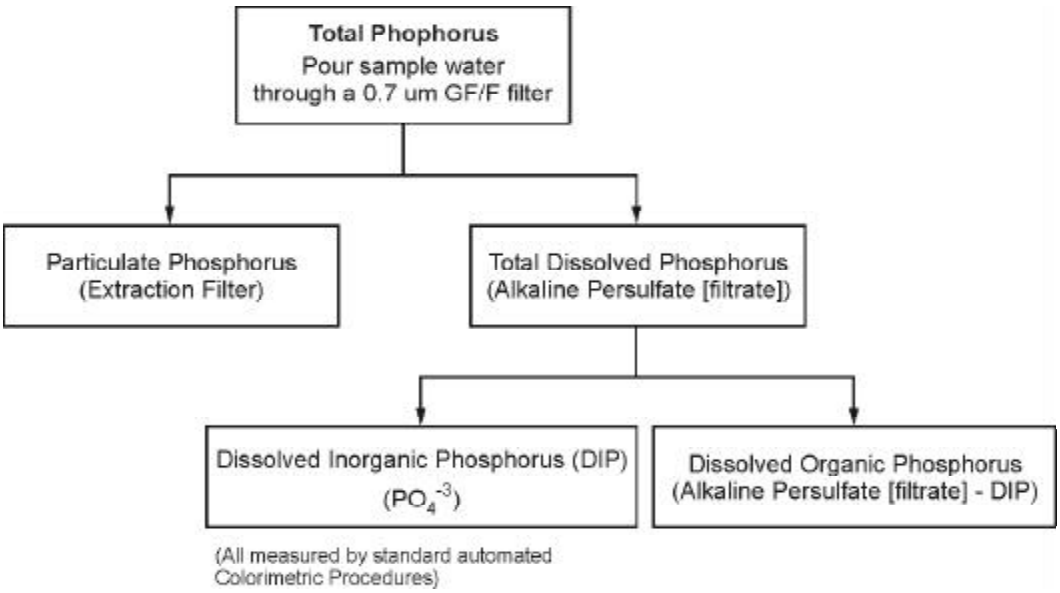
Figure 3.7 General Laboratory Procedures for Nitrogen Analyses.



Total Phosphorus is determined using an automated colorimetric analysis. Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex which is reduced to an intensely blue-colored complex by ascorbic acid. Color is measure at 880 nm using a Technicon Auto-Analyzer II. The color is proportional to phosphorus concentration. [Menzel, D.W. and N. Corwin, 1965. The Measurement of Total Phosphorus in Seawater Based on the Liberation of Organically Bound Fractions by Persulfate Oxidation. Limno. Oceanogr. 10:280-282 and USEPA. 1979. Method No. 365.3 *in* Methods for Chemical Analysis of Water and Wastes. United States Environmental Protection Agency, Office of Research and Development. Cincinnati, Ohio. Report No. EPA-600/4-79-020. March 1979.]

Total Inorganic Carbon (TIC) is determined by the measurement of carbon dioxide released by acidification of a sample. As pH decreases, carbonate and bicarbonate ions are converted to dissolved CO_2. The CO_2 is purged from solution, concentrated by trapping on a molecular sieve column, then desorbed and carried into a non-dispersive infrared analyzer (IR). The IR (OI Corp. Model 700 TOC Analyzer) is calibrated to display the mass of TIC in the sample divided by the sample volume. [Menzel, D.W. and R.F. Vaccaro. 1964. The Measurement of Dissolved Organic and Particulate Carbon in Seawater. Limnol. Oceanogr. 9:138-142]

Figure 3.8 General Laboratory Procedures for Phosphorus Analysis.



Total Organic Carbon (TOC) is determined by the measurement of CO_2 released by chemical oxidation of organic carbon in a sample. The sample is acidified and purged of TIC and sodium persulfate, a strong oxidizer, is added. The oxidant quickly reacts with organic carbon in the sample at 100˚C to form CO_2. When the oxidation reaction is complete, CO_2 is purged from solution, concentrated by trapping on a molecular sieve column and detected as described for TIC. [Methodology: Menzel and Vaccaro, 1964.]

Direct measurement of particulate carbon, nitrogen and phosphorus is the preferred method used by the Nutrient Analytical Services Laboratory (NASL). It is believed that a greater volume filtered onto the pad yields a more representative sample. Direct measurement is also rapid, sensitive and more precise.

For *Particulate Carbon and Nitrogen*, samples are combusted in pure oxygen under static conditions. Products of combustion are passed over suitable reagents in the combustion tube where complete oxidation occurs. In the reduction tube, oxides of nitrogen are converted to molecular nitrogen. The carbon dioxide, water vapor and

nitrogen are mixed and released into the thermal conductivity detector where the concentrations of the sample gases are measured. Instrumentation: CE-440 Elemental Analyzer.

Particulate Phosphorus is determined using a high temperature/HCl extraction technique where organic phosphorus is broken down to the inorganic form at 550˚C, extracted in 1N HCl for 24 hours and analyzed for phosphate using a Technicon AutoAnalyzer II. This is a total analysis where both inorganic and organic components are included. It has been determined that for Chesapeake Bay waters there is a varied and sometimes substantial inorganic particulate phosphorus component both temporally and spatially. [Aspila, I., H. Agemian and A.S.Y. Chau. 1976. A Semi-Automated Method for the Determination of Inorganic, Organic and Total Phosphate in Sediments. Analyst 101:187-197]

Total Suspended Solids (TSS) is the retained material on a standard glass filter pad after filtration of a well-mixed sample of water. The filtrate is measured and the filter is weighed. Results are expressed in mg/l. [APHA. 1975. Method 208D. Total Nonfilterable Residue Dried at 103-105 C (Total Suspended Matter) *in* Standard Methods for the Examination of Water and Wastewater, 14th Edition. American Public Health Association. Washington, D.C. 1193pp. and USEPA. 1979. Method No. 160.2 (with slight modification) *in* Methods for Chemical Analysis of Water and Wastes. United States Environmental Protection Agency, Office of Research and Development. Cincinnati, Ohio. Report No. EPA-600/4-79-020, March 1979. 460pp.]

Chlorophyll A is measured using a fluorometric method where a filter pad containing particulate material is extracted in 90% acetone in the cold and dark for 12 hours prior to analysis. Fluorescence of the extract is measured before and after acidification using a Turner Fluorometer Model 112. Fluorescence is proportional to Chlorophyll A concentration. [Strickland, J.D.H. and T.R. Parsons. 1972. A Practical Handbook of Seawater Analysis. Bulletin 167 (2nd Ed.). Fisheries Research Board of Canada, Ottawa, Canada. and Parsons, T.R., Y. Maita and C.M. Lalli. 1984. Determination of Chloropyhlls and Total Carotenoids: Spectrophotometric method. pp. 101-112 *in* Parsons, T.R., Y. Maita and C.M. Lalli. A Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, Oxford.]